Silylcarbene-to-Silene Rearrangement: Stable 1,2-Dihydrosilenes in Solution via the Silylcarbene Route

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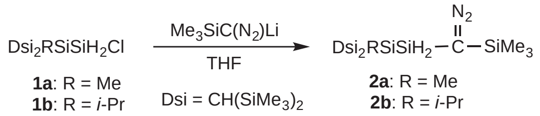
1,2-Dihydrosilenes were synthesized by the photolysis of silyldiazomethane derivatives bearing one bulky trialkylsilyl group $SiR[CH(SiMe_3)_2]_2$ (R = Me and *i*-Pr) and two hydrogen atoms on the silicon atom. The selective migration of the hydrogen atom to the carbene center occurred, leading to stable *trans*-1,2-dihydrosilenes, which were characterized by their spectroscopic data. An X-ray analysis of the Diels–Alder adduct demonstrated the trans geometry of the 1,2-dihydrosilene.

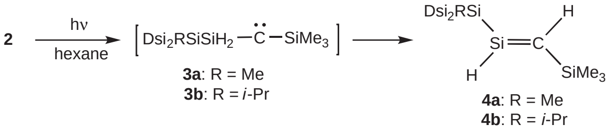
Since the isolation of the first stable silene ($>$Si=C$<$)[1] and disilene ($>$Si=Si$<$)[2] in 1981, much attention has been focused on the doubly bonded compounds of heavier group 14 elements.[3] The structural and chemical aspects of silenes are of particular interest, because they are known to differ from those of both alkenes $>$C=C$<$ and disilenes $>$Si=Si$<$ owing to the polar bond between the sp^2-silicon atom and the sp^2-carbon atom. A silene bearing hydrogen atoms on the sp^2-Si and sp^2-C atoms would be interesting in view of the fundamental chemistry of the silenes. The parent silene, $H_2Si=CH_2$,[4] was observed spectroscopically in an argon matrix at 10 K and its photoelectron spectrum (PE) has been obtained; however, its high reactivity made it impossible to measure important physical data such as the NMR coupling constants. Recently, we and Scheschkewitz, and Tokitoh's group independently reported stable hydrosilene derivatives, 1,1,2-tris(di-*tert*-butylmethylsilyl)-1,2-disilacyclobut-2-ene[5] and 1-hydrosilene {$Ar(H)Si=CAr'_2$; Ar = C_6H_2-2,4,6-$[CH(SiMe_3)_2]_3$, CAr'_2 = xanthenylidene};[6] the former has the $>$Si=CH– unit and the latter has the –HSi=C$<$ unit, from which the coupling constants $^1J_{C\text{–}H}$ and $^1J_{Si\text{–}H}$ were reported, respectively. We report here the first successful synthesis of 1,2-dihydrosilenes, a silene of the type –HSi=CH–, which enabled us to measure the coupling constants (both $^1J_{C\text{–}H}$ and $^1J_{Si\text{–}H}$, as well as $^3J_{H\text{–}Si=C\text{–}H}$).

Ando and Sekiguchi, and other groups have developed the chemistry of silylcarbenes over the past three decade.[7,8] Silylcarbenes, when generated by photochemical or thermal decomposition of silyldiazo compounds, rearrange to silenes by a 1,2-shift of the substituents, such as H, alkyl, alkenyl, aryl, and silyl groups.[8–10] All silenes generated so far via the silylcarbene route are reactive intermediates themselves, which have been characterized by trapping reactions and matrix isolation at low temperature.[7] However, there has been no previous stable silene in solution obtained by the silylcarbene route.

We have designed the silyldiazomethane derivatives **2** with one bulky trialkylsilyl $SiR[CH(SiMe_3)_2]_2$ group (**a**: R = Me, **b**: R = *i*-Pr) and two hydrogen atoms on the silicon atom. Silyldiazomethanes **2** were prepared as yellow oils by the reaction of the corresponding chlorosilanes **1** with the lithium salt of (trimethylsilyl)diazomethane in THF at −110 °C, as shown in Scheme 1.[11] Silyldiazo compounds **2** were purified by gel permeation chromatography (toluene as eluent) and used for the next photochemical reaction.



Scheme 1.

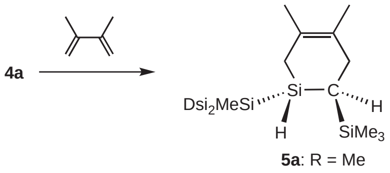


Scheme 2.

The photolysis of silyldiazomethanes **2** was carried out in hexane with a high-pressure mercury lamp ($\lambda > 350$ nm). Irradiation results in a decrease in the UV absorption of **2a** (374 nm) with concurrent formation of a new band with a maximum at 304 nm, due to the π–π^* transition of **4a**. The reactions were also followed by ^{1}H NMR spectroscopy, which showed the formation of silenes **4a** and **4b** in 29% and 47% yields, respectively (Scheme 2).[12] The formation of *trans*-1,2-dihydrosilenes **4** via hydrogen migration in silylcarbene intermediate **3** is selective, and other migration products were not detected. In general, the silyl group has a high migrating aptitude;[9c–9e] however, $SiR[CH(SiMe_3)_2]_2$ groups are extremely bulky, which prevents their migration to the carbene center for steric reasons.

Silene **4a** (R = Me) is stable in C_6D_6 solution at 0 °C, but slowly decomposes at room temperature (ca. 50% decomposition after one week). Silene **4b** (R = *i*-Pr) is stable in C_6D_6 solution at room temperature and no decomposition was observed after prolonged standing. Several attempts to crystallize **4b** were unsuccessful. The structures of **4a** and **4b** have been confirmed by ^{1}H, ^{13}C, ^{29}Si NMR, and mass spectra, as well as by product analysis of the trapping reaction. *trans*-1,2-Dihydrosilenes **4** show characteristic ^{13}C and ^{29}Si NMR signals assignable to sp^2-carbon and sp^2-silicon atoms: 129.1 (^{13}C) and 119.5 ppm (^{29}Si) for **4a**, and 129.0 (^{13}C) and 116.1 ppm (^{29}Si) for **4b**. Comparing the chemical shifts of the sp^2-silicon of disilenyllithium {*trans*-$R'(H)\mathit{Si}=Si(Li)R'$; R' = Si-*i*-Pr$[CH(SiMe_3)_2]_2$}[13] (δ_{Si} 124.7) and the sp^2-carbon of trimethylvinylsilane ($Me_3Si\mathit{C}H=CH_2$)[14] (δ_C 140.3) shows that the shifts of dihydrosilene **4b** are reasonable.

It is important to note that the half-parent system **4** offers the unprecedented possibility of studying the NMR coupling constant between two hydrogen atoms directly attached to both the silicon and the carbon atoms of the $>$Si=C$<$ bond. In the



Scheme 3.

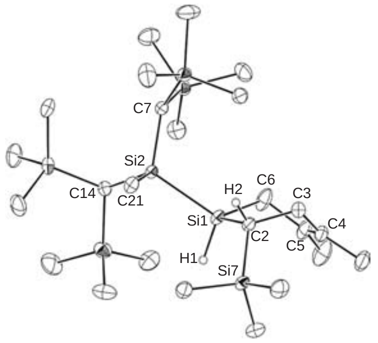


Figure 1. ORTEP drawing of **5a** (30% probability level). Hydrogen atoms except for H1 on Si1 and H2 on C2 are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Si1–Si2 = 2.3981(5), Si1–C2 = 1.9058(16), Si1–C6 = 1.8927(18), Si7–C2 = 1.8857(15), Si2–C7 = 1.9049(14), Si2–C14 = 1.9065(15), Si2–Si1–C2 = 115.05(5), Si2–Si1–C6 = 119.22(6), C2–Si1–C6 = 101.66(8).

^{1}H NMR spectra of **4**, the hydrogen atoms on the silene moiety were observed at 5.86 and 6.41 ppm for **4a** and 5.79 and 6.28 ppm for **4b**. The former signal is assignable to the hydrogen atom on the sp^2-silicon [^1J (Si–H) = 189 Hz for **4a** and ^1J (Si–H) = 190 Hz for **4b**] and the latter signal is assignable to the hydrogen atom on the sp^2-carbon [^1J (C–H) = 133 Hz for **4a** and ^1J (C–H) = 133 Hz for **4b**]. These chemical shifts are similar to those of the hydrogen atoms on the sp^2-silicon atom of 1-hydrosilene {Ar(*H*)Si=CAr′$_2$; Ar = C_6H_2-2,4,6-[CH(SiMe$_3$)$_2$]$_3$, CAr′$_2$ = xanthenylidene}[6] (δ_H 6.06), but are at a much higher field compared with that of the sp^2-carbon atom of 1,1,2-tris(di-*tert*-butylmethylsilyl)-1,2-disilacyclobut-2-ene (δ_H 7.47).[5] Both signals are split into doublets by coupling to each other, and their $^3J_{\text{H–Si=C–H}}$ coupling constants are 15.0 Hz for **4a** and 15.1 Hz for **4b**, indicating a trans geometry for H–Si=C–H. This value is smaller than that of the $^3J_{\text{H–C=C–H}}$ of the *trans*-H–C=C–H moiety (cf. 20.1 Hz for trimethylvinylsilane[14]) by ca. 5 Hz.

To confirm the geometry of the silene, we examined the reaction of **4a** with 2,3-dimethyl-1,3-butadiene. Thus, 1,2-dihydrosilene **4a** readily reacts with 2,3-dimethyl-1,3-butadiene to form the Diels–Alder cycloadduct **5a** quantitatively (Scheme 3). Although silenes react rapidly with dienes by [2 + 4] cycloaddition and/or ene-reaction, only cycloadduct **5a** was isolated in this case.[15] The structure of **5a** was confirmed by X-ray diffraction analysis, which supports the contention that silenes have the trans geometry, as shown by the ORTEP drawing of **5a** (Figure 1).

References and Notes

1 A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, *J. Chem. Soc., Chem. Commun.* **1981**, 191.

2 R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343.

3 a) L. E. Gusel'nikov, N. S. Nametkin, *Chem. Rev.* **1979**, *79*, 529. b) G. Raabe, J. Michl, *Chem. Rev.* **1985**, *85*, 419. c) M. A. Chaubon, H. Ranaivonjatovo, J. Escudié, J. Satgé, *Main Group Met. Chem.* **1996**, *19*, 145. d) A. G. Brook, M. A. Brook, *Adv. Organomet. Chem.* **1996**, *39*, 71. e) T. Müller, W. Ziche, N. Auner, in *The Chemistry of Organosilicon Compounds*, ed. by Z. Rappoport, Y. Apeloig, Wiley, New York, **1998**, Vol. 2, Part 2, Chap. 16. f) T. L. Morkin, W. J. Leigh, *Acc. Chem. Res.* **2001**, *34*, 129. g) L. E. Gusel'nikov, *Coord. Chem. Rev.* **2003**, *244*, 149. h) H. Ottosson, P. G. Steel, *Chem.—Eur. J.* **2006**, *12*, 1576. i) H. Ottosson, A. M. Eklöf, *Coord. Chem. Rev.* **2008**, *252*, 1287.

4 For the argon matrix isolation, see: a) G. Maier, G. Mihm, H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 597. For PE spectrum, see: b) P. Rosmus, H. Bock, B. Solouki, G. Maier, G. Mihm, *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 598.

5 I. Bejan, S. Inoue, M. Ichinohe, A. Sekiguchi, D. Scheschkewitz, *Chem.—Eur. J.* **2008**, *14*, 7119.

6 S. Ozaki, T. Sasamori, N. Tokitoh, *Organometallics* **2008**, *27*, 2163.

7 G. Maas, in *The Chemistry of Organic Silicon Compounds*, ed. by Z. Rappoport, Y. Apeloig, Wiley, Chichester, U.K., **1998**, Vol. 2, Chap. 13.

8 a) W. Ando, T. Hagiwara, T. Migita, *J. Am. Chem. Soc.* **1973**, *95*, 7518. b) W. Ando, A. Sekiguchi, T. Hagiwara, T. Migita, V. Chowdhry, F. H. Westheimer, S. L. Kammula, M. Green, M. Jones, Jr., *J. Am. Chem. Soc.* **1979**, *101*, 6393. c) A. Sekiguchi, W. Ando, *Chem. Lett.* **1983**, 871. d) A. Sekiguchi, W. Ando, *Chem. Lett.* **1986**, 2025. e) A. Sekiguchi, W. Ando, *Organometallics* **1987**, *6*, 1857.

9 M. Trommer, W. Sander, A. Patyk, *J. Am. Chem. Soc.* **1993**, *115*, 11775.

10 W. J. Leigh, C. Kerst, R. Boukherroub, T. L. Morkin, S. I. Jenkins, K. Sung, T. T. Tidwell, *J. Am. Chem. Soc.* **1999**, *121*, 4744.

11 **2a**: deep yellow oil, ^{1}H NMR (C_6D_6, δ): −0.11 (s, 2H), 0.16 (s, 9H), 0.22 (s, 18H), 0.29 (s, 18H), 0.71 (s, 3H), 4.31 (s, 2H); ^{13}C NMR (C_6D_6, δ): −1.0, 4.3, 4.5, 4.9, 5.6, 10.5; ^{29}Si NMR (C_6D_6, δ): −60.3, −9.9, −0.3, 0.3, 4.0; IR (KBr): 2047 (C=N$_2$) cm^{-1}; UV–vis $\lambda_{\max}$/nm (hexane, ε): 258 (4000), 374 (30); HRMS (APCI): *m*/*z* cald for $C_{19}H_{53}N_2Si_7$ 505.2588 [M + H]$^+$, found 505.2588. **2b**: ^{1}H NMR (C_6D_6, δ): −0.04 (s, 2H), 0.15 (s, 9H), 0.27 (s, 18H), 0.31 (s, 18H), 1.28 (d, J = 7.0 Hz, 6H), 1.53 (sep, J = 7.0 Hz, 1H), 4.32 (s, 2H); ^{13}C NMR (C_6D_6, δ): −1.1, 5.2, 5.3, 6.8, 10.5, 17.0, 21.4; ^{29}Si NMR (C_6D_6, δ): −61.0, −0.4, −0.1 (Dsi × 2), 4.1; IR (KBr): 2045 (C=N$_2$) cm^{-1}; UV–vis $\lambda_{\max}$/nm (hexane, ε): 254 (3600), 375 (80); HRMS (APCI): *m*/*z* cald for $C_{21}H_{57}N_2Si_7$ 533.2901 [M + H]$^+$, found 533.2901.

12 **4a**: ^{1}H NMR (C_6D_6, δ): −0.20 (s, 2H), 0.18 (s, 18H), 0.25 (s, 18H), 0.31 (s, 9H), 0.66 (d, J = 1.0 Hz, 3H), 5.86 (dd, J = 15.0 Hz, 1.0 Hz, 1H), 6.41 (d, J = 15.0 Hz, 1H); ^{13}C NMR (C_6D_6, δ): 3.2, 3.8 (Dsi × 2), 4.5, 5.0, 129.1 (Si=C), ^1J (C_{sp2}–H) = 133 Hz; ^{29}Si NMR (C_6D_6, δ): −6.9, −0.4 (Dsi × 2), 0.5, 119.5 (Si=C), ^1J (Si–H) = 189 Hz, HRMS (APCI): *m*/*z* cald for $C_{19}H_{52}Si_7$ 476.2448 (M$^+$), found 476.2444. **4b**: ^{1}H NMR (C_6D_6, δ): −0.08 (s, 2H), 0.23 (s, 18H), 0.29 (s, 18H), 0.31 (s, 9H), 1.23 (d, J = 7.0 Hz, 6H), 1.45 (sep, J = 7.0 Hz, 1H), 5.79 (d, J = 15.1 Hz, 1H), 6.28 (d, J = 15.1 Hz, 1H); ^{13}C NMR (C_6D_6, δ): 2.3, 5.1, 5.5, 6.0, 17.0, 21.8, 129.0 (Si=C), ^1J (C_{sp2}–H) = 133 Hz; ^{29}Si NMR (C_6D_6, δ): −6.9, −0.1, 0.1, 0.4, 116.1 (Si=C), ^1J (Si–H) = 190 Hz; HRMS (APCI): *m*/*z* cald for $C_{21}H_{56}Si_7$ 504.2761 (M$^+$), found 504.2761.

13 R. Kinjo, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2007**, *129*, 26.

14 A. Pollex, M. Hiersemann, *Org. Lett.* **2005**, *7*, 5705.

15 **5a**: Mp: 81–82 °C. ^{1}H NMR (C_6D_6, δ): −0.14 (s, 1H), −0.07 (s, 1H), 0.17 (s, 9H), 0.24 (s, 9H), 0.26 (s, 9H), 0.27 (s, 9H), 0.30 (s, 9H), 0.54–0.55 (m, 1H) (C–H), 0.57 (s, 3H), 1.62–1.69 (m, 2H) (Si–CH$_2$), 1.71 (s, 3H, C=C–Me), 1.76 (s, 3H, C=C–Me), 2.31 (d, J = 15.1 Hz, 1H) (C–CH$_2$), 2.53 (d, J = 15.1 Hz, 1H) (C–CH$_2$), 4.10 (s, 1H) (Si–H); ^{13}C NMR (C_6D_6, δ): −0.4, 4.58, 4.61, 4.7, 4.8, 5.3, 5.5, 5.9, 6.3, 17.5 (Si–CH$_2$), 21.6, 22.4, 32.3 (C–*C*H$_2$), 126.9 (*C*=*C*), 128.7 (*C*=*C*). ^{29}Si NMR (C_6D_6, δ): −36.1 (Si–H), −12.1, −0.54, −0.49, 0.11, 0.14, 4.7. HRMS (APCI): *m*/*z* cald for $C_{25}H_{63}Si_7$ 559.3309 [M + H]$^+$, found 559.3310. Crystal data for **5a** at 150 K: $C_{25}H_{62}Si_7$, M_r 559.38, Triclinic, $P\bar{1}$, a = 11.0830(2), b = 12.2080(4), c = 15.7180(5) Å, α = 102.929(2), β = 104.864(2), γ = 109.431(2)°, V = 1823.57(9) Å^3, Z = 2, D_{calcd} = 1.019 g cm^{-3}, R = 0.0406 ($I > 2\sigma(I)$), R_w = 0.1201 (all data), GOF = 1.007.